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A PROGRESS REPORT

CMB-13 Research on Carbon and Graphite

Report No. 19

Summary of Progress from August 1 to October 31, 1971

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This report presents the summary of progress of CMB-13 research on carbon and graphite at LASL. The four most recent reports in this series, all unclassified, are:

LA-4631-MS
LA-4714-MS

LA-4770-MS
LA-4896-PR

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Summary of Progress from August 1 to October 31, 1971*

by

Morton C. Smith

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of the National Aeronautics and Space Administration.

CMB-13 RESEARCH ON CARBON AND GRAPHITE
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I. INTRODUCTION

This is the nineteenth in a series of progress reports devoted to carbon and graphite research in LASL Group CMB-13, and summarizes work done during the months of August, September, and October, 1971. It should be understood that in such a progress report many of the data are preliminary, incomplete, and subject to correction, and many of the opinions and conclusions are tentative and subject to change. This report is intended only to provide up-to-date background information to those who are interested in the materials and programs described in it, and should not be quoted or used as a reference publicly or in print.

Research and development on carbon and graphite were undertaken by CMB-13 primarily to increase understanding of their properties and behavior as engineering materials, to improve the raw materials and processes used in their manufacture, and to learn how to produce them with consistent, predictable, useful combinations of properties. The approach taken is microstructural, based on study and characterization of natural, commercial, and experimental carbons and graphites by such techniques as x-ray diffraction, electron and optical microscopy, and porosimetry. Physical and mechanical properties are measured as functions of formulation, treatment, and environmental variables, and correlations are sought among properties and structures. Raw materials and manufacturing techniques are investigated, improved, and varied systematically in an effort to

create specific internal structures believed to be responsible for desirable combinations of properties. Prompt feedback of information among these activities then makes possible progress in all of them toward their common goal of understanding and improving manufactured carbons and graphites.

Since its beginning, this research has been sponsored by the Division of Space Nuclear Systems of the United States Atomic Energy Commission, through the Space Nuclear Propulsion Office. More recently additional general support for it has been provided by the Office of Advanced Research and Technology of the National Aeronautics and Space Administration. Many of its facilities and services have been furnished by the Division of Military Application of AEC. The direct and indirect support and the guidance and encouragement of these agencies of the United States Government are gratefully acknowledged.

II. SANTA MARIA COKE

A. Previous Work

Santa Maria coke and the nearly isotropic graphites made from it have previously been discussed in Reports 9 through 18 in this series.

B. Effects of Grinding (J. A. O'Rourke)

In evaluating the crystalline perfection of coarse filler materials, it has been customary to grind the filler to a fine particle size prior to packing it into the x-ray sample holder. This practice is open to question, since the introduction of residual stresses or crystalline

TABLE I
CRYSTALLINE PARAMETERS OF GROUND AND UNGROUND SANTA MARIA GRAPHITE FLOURS

Grind (a)	Size Fraction	Diffractometer #1		Diffractometer #2	
		L_c (Å)	d_{002} (Å)	L_c (Å)	d_{002} (Å)
As-received	-100 + 140 mesh	348	3.369	345	3.370
As-received	-140 + 200 mesh	349	3.370	350	3.370
As-received	-200 + 270 mesh	349	3.370	349	3.370
As-received	-270 + 400 mesh	351	3.369	354	3.369
As-received	- 400 mesh	350	3.368	353	3.368
Grind #1	-100 + 140 mesh	349	3.369	353	3.368
Grind #1	-200 + 270 mesh	355	3.367	354	3.367
Grind #1	- 400 mesh	358	3.367	360	3.367
Grind #2	- 400 mesh	354	3.367	353	3.367
Grind #3	---	317	3.368	318	3.367
Grind #4	---	312	3.367	316	3.367
Grind #4 (b)	---	326	3.367	333	3.367

(a) Grind #1: +100 fraction from As-received material, lightly ground for 20 minutes.

Grind #2: +100 fraction from Grind #1, further ground until all just -400 mesh.

Grind #3: Grind #2 material, further heavily ground for 1/2 hour.

Grind #4: +100 fraction from As-received material, ground as a water slurry in a ball mill for 4.5 days.

(b) "Amorphous" background subtracted.

imperfections into the filler by the grinding operation could change the profiles and positions of x-ray diffraction lines, and thus produce significant errors in measurements of the crystalline parameters. To resolve this question, the crystalline perfections of several size fractions of a Santa Maria graphite flour were determined. Then the coarsest fraction was ground in a Spex Mixer/Mill and finally in a ball mill, in controlled steps, to a very fine particle size. Samples for x-ray examination were taken after each of four grinding steps. The crystalline parameters of each of these samples and of various size-fractions of the original flour are listed in Table I. Each value listed is the average of at least five separate determinations, and, as is indicated in the table, the samples were run on two diffractometers which differed with regard to instrumental broadening. There was excellent agreement in the results from the two diffractometers.

Within the estimated experimental error, which is 2 to 3% for L_c and 0.03% for d_{002} , there were no significant differences among the five size fractions of the as-received material, the three size fractions of Grind No. 1, and Grind No. 2. Significant line broadening was observed only for Grinds 3 and 4, which were very heavily ground, and here it is believed that an actual reduction in crystallite size is being observed rather than an effect of residual stress. In Grind No. 4 a contribution was observed near the base of the diffraction peaks, which apparently resulted from the production of a small proportion of nearly amorphous carbon during extremely fine grinding. Measurements of the crystalline parameters were made both with and without subtraction of this component, and both results are listed in the table. Even without subtraction of the weak amorphous contribution, there was little or no further line broadening over that previously observed for Grind No. 3.

TABLE II

DENSITY AND SHRINKAGE PROPERTIES OF RESIN-BONDED HOT-MOLDED GRAPHITES

Specimen No.	Binder Viscosity, cp	Binder Conc., pph	Calculated Binder Optimum, pph	Binder Residue						Density, g/cm ³						Dimen. Chg., %, Cured to Graph.		
				% of total			Concentration, (a) g/cm ³			Packed Filler			Bulk			ΔL	Δd	Δv
				Cured	Baked	Graph.	Cured	Baked	Graph.	Cured	Baked	Graph.	Cured	Baked	Graph.			
80A-2 ^(b)	5×10^4	30	24.1	79.2	---	47.8	1.16	---	0.96	1.451	---	1.583	1.802	---	1.814	-2.8	-2.9	-8.4
80D-1 ^(b)	1.3×10^4	30	22.5	78.0	43.2	42.3	1.22	0.86	0.89	1.481	1.576	1.601	1.834	1.783	1.808	-2.1	-2.8	-7.5
80E-1 ^(c)	1.3×10^4	22	19.0	87.3	52.3	51.1	1.19	0.81	0.83	1.551	1.601	1.618	1.854	1.789	1.803	-0.6	-1.8	-4.1
80B-1 ^(d)	7.5×10^3	30	18.3	62.5	33.2	32.2	1.20	0.68	0.75	1.564	1.589	1.638	1.864	1.799	1.799	-0.8	-1.9	-4.5
80C-1 ^(d)	7.7×10^2	30	17.6	55.3	31.4	30.2	1.11	0.70	0.70	1.579	1.618	1.633	1.846	1.773	1.784	-0.5	-1.4	-3.3

(a) Grams of binder-coke per cm³ of available void space.

(b) After molding (pressure-cure), specimen surface had a "wormy" appearance. Radial cracks developed after baking.

(c) Lamination-type crack part way through the specimen developed on graphitizing.

(d) Diametral crack developed during molding (pressure-cure).

To the point at which actual fragmentation of crystallites becomes significant, it appears that even very fine grinding of a Santa Maria graphite flour has no effect on the crystalline parameters measured by x-ray diffraction. In fact, the results listed in Table I suggest that the initial reductions may slightly improve crystallite perfection. This could be explained in terms of the relief of residual stresses initially present in the coarser particles. However, in this case the differences are small enough to be explained simply by experimental error.

C. Resin-Bonded Graphites (R. J. Imprescia)

Furfuryl alcohol resins have been used very successfully as binders in the manufacture of small-diameter extruded graphite rods. In the manufacture of hot-molded graphites, however, their success has been marginal. Even the better molded resin-bonded materials have been found to contain numerous highly aligned microcracks. An investigation has therefore been undertaken of the manufacturing variables that may be involved in this cracking behavior.

As the first step in the investigation, the three hot-molded graphites identified in Table II as 80A-2, 80B-1, and 80C-1 were made from Santa Maria Lot G-26 graphite flour and 30 pph of each of three experimental furfuryl alcohol resin binders. The three binders differed widely in viscosity, and the purpose of the series was to determine the effect of binder viscosity on compaction behavior of the filler. Comparison of the density data listed

in Table II with similar data from previous experiments suggested that a binder with viscosity in the range 10,000 to 20,000 cp might be more suitable than any of those selected initially. Accordingly, a fourth binder, with viscosity of 13,000 cp was used to make two more specimens. Specimen 80D-1 contained 30 pph of binder, as did the previous specimens, but in Specimen 80E-1 binder concentration was reduced to 22 pph.

All raw mixes were prepared by standard mixing and chopping processes. Specimens were molded and pressure-cured in graphite dies at 2000 psi, which was maintained during heating to 200°C at 2.5°C/hr. It was found necessary to hold the specimens for several hours at 200°C before releasing pressure; otherwise unevolved gases caused laminar cracks to form when pressure was released. In all previous hot-molding of resin-bonded graphites, pressure has been maintained during baking. With these specimens pressure was released after curing at 200°C, and baking was done in vacuum or in atmospheric-pressure argon, at 13.5°C/hr to 900°C. All specimens were graphitized in helium to 2800°C, with the following heating schedule: 20 to 900°C at 400°C/hr; 900 to 1500°C at 200°C/hr; 1500 to 2200°C at 300°C/hr; 2200 to 2800°C at 400°C/hr; hold 1/2 hr at 2800°C; furnace-cool.

Each of these specimens developed manufacturing defects of some kind. Specimen 80A-2, made from the highest-viscosity (50,000 cp) binder had the greatest

TABLE III
PROPERTIES OF GRADES 30M AND 30MH COAL-TAR PITCHES^(a)

	Grade 30M	Grade 30MH
Softening point, cube-in-air method	98-103°C	108-113°C
Density at 25°C	1.29-1.35 g/cm ³	1.30-1.36 g/cm ³
Benzol insolubles	27-35%	28-36%
Quinoline insolubles	10-16%	10-16%
Coking value, Conradson	50% min	52% min
Ash	0.25% max	0.25% max

(a) Technical Data Report, CP 277, 10-20-66, Plastics Division, Allied Chemical Corporation.

graphitized bulk density and carbon-residue concentration, although its packed filler densities were the lowest in the series. It had a peculiar "wormy" surface after pressure-curing, which persisted through baking and graphitizing. Apparently the binder lacked lubricity, explaining the poor particle packing, and did not become fluid enough during compaction to eliminate the interfaces between the spaghetti-like pieces of conditioned mix produced by the food-chopper.

Specimens 80B-1 and 80C-1 cracked during molding. They were quite similar in densities and, except for the cracks, looked like good graphites. Their high-packed filler densities indicate that the lubricities of the 770 and 7500 cp resins used to make them were adequate for a molding operation.

Because of a difference in binder concentration, the two specimens made with the 13,000 cp resin were quite different in appearance. Specimen 80D-1, which had 30 pph binder, had a slightly "wormy" surface, of the type described above, and developed serious radial cracks during baking. Specimen 80E-1, with only 22 pph binder, had no surface defects or radial cracks, but developed one circumferential crack which was continuous around the cylindrical surface of the specimen.

During machining of test bars from these samples, it was observed that all of them had numerous internal cracks, which were large enough to be seen without magnification. Evidently a serious fabrication problem

exists even when a very good furfuryl alcohol resin binder is used.

The next step in this program will be to examine the effect on cracking of variations in the temperature-pressure cycles during molding.

III. RAW MATERIALS

A. Kynol Fibers (R. J. Imprescia, R. D. Reiswig)

Kynol is a phenolic fiber which has been used as a reinforcing addition to a variety of pitch-bonded highly oriented graphites. Added to the raw mix as the green (uncarbonized) fiber, it usefully enhances certain properties of such graphites, including their with-grain thermal conductivities and flexure strengths. However, the behavior of Kynol in producing this enhancement is not well understood, in particular because it is very difficult to locate and identify the fiber residue in the structure of the finished graphite.

As was discussed in Report No. 12 in this series, Kynol fibers, when hot-molded by themselves, appear to fuse into a highly fragmented mass of dense particles, which exhibit a high degree of optical anisotropy. However, an attempt to use Kynol as a binder for natural graphite, described in Report No. 13, was not particularly successful. In these graphites the residues of the individual Kynol fibers were observable under the microscope. They were oval in section, indicating that they had deformed during compaction (which is the principal advantage of using a green rather than a carbonized

fiber). However, associated with each fiber was a parallel void almost as large as the fiber residue itself, evidently produced by shrinkage of the fiber during pyrolysis. There was no obvious bonding between filler particles and fibers, and the finished graphites contained many laminar microcracks that apparently originated at these shrinkage voids.

The suggestion was made that the enhancement of properties which occurred when both Kynol and pitch were present might result from some interaction between the two. To explore this possibility, Kynol fibers were stirred into a beaker of molten 30MH pitch at about 150°C, then heated slowly to 270°C and held for 5 min. Subsequent microscopic examination of the cooled mass showed no interaction except wetting of the fibers by the pitch. The nominal 14 μ diameter of the fibers was unchanged.

A mixture of equal parts by weight of Kynol fiber and 30MH pitch was molded at 2000 psi, and heated under this pressure to 700°C. Again, after cooling to room temperature, the fibers were slightly deformed but apparently had simply been wetted by the pitch. There was no evidence of reaction or dissolution of the fibers. Microscopic examination showed a high degree of optical anisotropy in the hot-molded material, probably due to alignment of the molecular structure of the Kynol during fiber manufacture.

No evidence was found of any unusual interaction between the Kynol fibers and a coal-tar pitch binder. Apparently the fiber residue is simply bonded into the graphite structure more effectively when it is associated with a fluid binder that wets it than when it is used alone.

B. Properties and Purities of Coal-Tar Pitches (R. J. Imprescia)

Until very recently, the standard binder used in the manufacture of CMB-13 molded graphites was Barrett Grade 30MH coal-tar pitch. Because this grade is no longer commercially available, it has been replaced by Grade 30M pitch, which will be considered the standard binder for future CMB-13 pitch-bonded materials.

The general properties of these two pitches, as reported by their manufacturer, are listed in Table III.

Their impurity contents, as-received and after baking at 900°C, are listed in Table IV. So far as these analyses indicate, the two pitches are very much alike. However, Grade 30M has a slightly lower softening point and slightly higher purity than Grade 30MH and presumably graphitizes somewhat more readily.

C. Carbonization of Resin Components (E. M. Wewerka, E. D. Loughran)

The mass spectra of several furfuryl-alcohol-resin components were discussed in Report No. 17 in this series. Particular attention was given to the proportion of tropylium ion formed from each component during electron-impact fragmentation in the mass spectrometer. This ion is the gas-phase equivalent of the benzyl ion, which is believed to be a principal precursor for formation of higher-molecular-weight compounds. It was therefore suggested that the proportion of tropylium ion formed by electron-impact fragmentation might correlate with the graphitizing tendency of the carbon residue produced by pyrolysis of a particular resin component.

To examine this possibility, gas chromatography was used to separate approximately 0.5 g quantities of each of the following resin components: furfuryl alcohol; difurylmethane; difurfuryl ether; difurfuryl furan; and 5-furfurylfurfuryl alcohol. A trace amount of maleic anhydride catalyst was added to each sample, and it was then cured, baked, and graphitized to 2800°C in standard heat-treating cycles. The resulting carbons were examined by x-ray diffraction methods by J. A. O'Rourke, CMB-13.

As was described in Report No. 17, these resin components exhibit a variety of fragmentation behaviors when subjected to electron bombardment, particularly with regard to their yields of tropylium ion. However all of them, after carbonization and heat-treatment to 2800°C, were found to yield essentially indistinguishable, nearly amorphous carbons, whose L_c values ranged only from 23.9 to 27.9 Å.

There appears to be no relation between the behaviors of these compounds when they are fragmented by electron impact and those observed when they are carbonized thermally. Therefore, no further work in this area is planned.

TABLE IV
IMPURITIES IN COAL-TAR PITCHES^(a)

Element	Grade 30M		Grade 30MH	
	As-Received	Coked, 900°C	As-Received	Coked, 900°C
S	0.23%	0.20%	0.25%	0.25%
Fe	120	160	340	430
Li	<10	<10	<10	<10
Be	< 1	< 1	< 1	< 1
B	< 1	< 1	< 1	< 1
Na	200	300	200	400
Mg	15	15	15	15
Al	100	100	200	200
Si	200	200	200	200
K	<50	60	100	60
Ca	100	100	40	100
Ti	40	<10	<10	<10
V	<10	<10	<10	<10
Cr	<10	<10	<10	<10
Mn	< 3	< 3	3	3
Ni	<10	<10	<10	<10
Cu	< 3	< 3	< 3	5
Zn	50	60	50	70
Sr	< 5	< 5	< 5	< 5
Zr	<10	20	<10	<10
Nb	<10	<10	<10	<10
Mo	<10	<10	<10	<10
Cd	< 1	< 1	< 1	< 1
Sn	<10	<10	<10	<10
Ba	< 5	< 5	< 5	< 5
Pb	40	40	40	40
Bi	<10	<10	<10	<10
Ash	0.25%	0.34%	0.31%	0.43%

(a) In ppm unless indicated otherwise. Concentrations of S, Fe, and Ash were determined by conventional quantitative analyses. All other concentrations were estimated by semi-quantitative spectro-chemical analyses. All analyses by LASL Group CMB-1.

D. Synthesis of γ -BL (E. M. Wewerka, R. J. Barreras)

As has been reported, the first two steps in the independent synthesis of 4-furfuryl-2-pentenoic acid- γ -lactone (" γ -BL") have been well worked out, and are producing satisfactory yields of 2-furaldehyde and

α -furylacetone. The final intermediate compound, 3-furfuryl-3-hydroxy-1-butyne, has also been successfully synthesized in low yield. However, the final step in the synthesis -- conversion of this third intermediate to γ -BL -- has not yet been accomplished.

Because of low yields of the final intermediate and the difficulties encountered in the last synthetic step, a model compound instead of the actual intermediate is now being used to investigate the experimental conditions required to produce γ -BL. This compound is 3-methyl-3-hydroxy-1-butyne, which is easily obtained in good yield by reaction of an acetylide salt with acetone. It is similar in structure to 3-furfuryl-3-hydroxy-1-butyne, and is expected to exhibit similar chemical behavior.

Using this model compound, two alternative synthetic routes have been investigated for the final step of the reaction sequence. One, utilizing nickel carbonyl, is a one-step procedure which has been reported in the literature for compounds similar to γ -BL. The other uses a Grignard reagent. Several alternative experimental conditions have been tried for each procedure, including a Grignard reaction in the presence of CO_2 in a stainless-steel pressure bomb. No yield of the desired reaction product has so far been detected.

E. Glass-Like Carbon Filler (H. D. Lewis, J. A.

O'Rourke)

A glass-like carbon powder has been prepared by LASL Group CMB-6 and will be used by CMB-13 as a filler material in the manufacture of various special carbons and carbon-graphites. It was produced by casting

a large quantity of Varcum 8251 furfuryl alcohol resin, curing and baking the polymer, and graphitizing the carbon residue to 2500°C. The resulting glass-like carbon was ground in the CMB-6 sample-pulverizing mill to a fineness of 30.6% by weight less than 325 mesh. Probably as a result of iron pickup from the grinding mill, it contained 0.20% Fe. A small lot of the material was acid-leached by CMB-13, reducing its iron content to 100 ppm. This leached material is identified as CMB-13 Lot C(VC)-13.

As-received from CMB-6 the glass-like carbon flour had helium density of 1.506 g/cm³ and crystalline parameters of $L_c = 24.6 \text{ \AA}$, $d_{002} = 3.45 \text{ \AA}$. After leaching the values were 1.496 g/cm³, $L_c = 24.4 \text{ \AA}$, and $d_{002} = 3.44 \text{ \AA}$. Apparently the iron was present as surface contamination on the particles, and no significant disruption of particle structures was produced by the leaching operation.

Particle characteristics of the leached C(VC)-13 flour are listed in Table V, and micromerograph particle-size data are plotted in Fig. 1. The particle density is typical of a glass-like carbon, which apparently contains a great deal of very fine closed porosity. The x-ray parameters are also typical, and indicate a very highly disordered structure, even after heat-treatment to 2500°C. The particle-size distribution is very far from lognormal, but may be characteristic of the mill used to grind the material rather than of the material itself. The variance and coefficient of variation of the distribution are quite high, indicating that the filler will probably pack quite efficiently. Measured (BET) specific surface area and fuzziness ratio are higher than might be expected for compact particles with essentially no surface-connected porosity. This is probably because, like a true glass, the glass-like carbon tends to break into angular shards with a relatively large amount of surface.

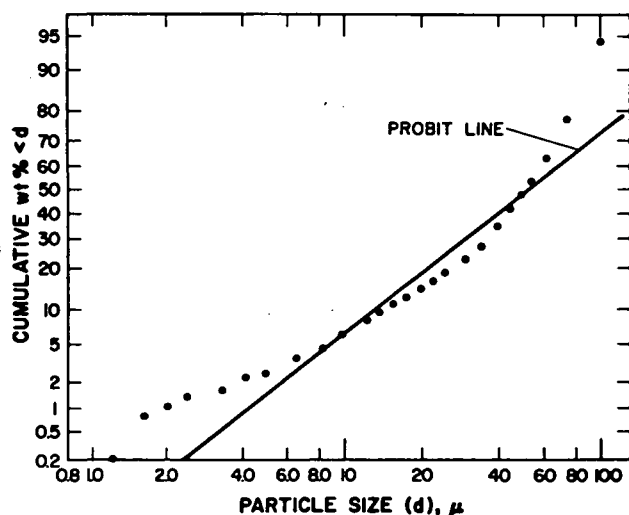


Fig. 1. Log-probability plot of micromerograph particle-size data for glass-like carbon filler, Lot C(VC)-13.

TABLE V
PARTICLE CHARACTERISTICS
OF GLASS-LIKE CARBON FILLER, LOT C(VC)-13

Helium density	1.496 g/cm ³
Crystalline parameters	
L_c	24.4 Å
d_{002}	3.44 Å
Micromerograph sample statistics ^(a)	
Mean dia, \bar{d}_3	52.38 μ
Variance, $s_{d_3}^2$	777.4 μ^2
Calc. surface area, S_W	0.1595 m ² /g
Coeff. of Variation, CV_d	1.30
BET surface-area data	
Surface area, S_W	9.56 m ² /g
Dia of equivalent sphere, d_s ^(b)	0.420 μ
Fuzziness ratio, R_F ^(c)	59.94

(a) Interval model.

(b) $d_s = 6/\rho S_W$.

(c) $R_F = S_W$ (BET) S_W (Calc)

IV. HYDROGEN CONTENTS OF COMMERCIAL COKES AND GRAPHITES

(R. J. Imprescia, J. A. O'Rourke)

On the basis of his mass-spectrometric studies of vapor species evolved from heated carbons and graphites, R. T. Meyer of the Sandia Laboratories, Albuquerque, New Mexico, has postulated an effect of hydrogen content on the ablation behavior and other mass-removal properties of carbon-base materials. However, very little information has been found in the literature on the hydrogen contents of carbons and graphites. Therefore, in cooperation with Dr. Meyer, hydrogen analyses have been made on a series of cokes and graphites of known history or of special interest to Dr. Meyer's programs. These data are summarized in Table VI, together with available information on the crystalline parameters of the samples analyzed. The latter values are included because it has

been suggested that its hydrogen content may directly affect the degree of crystallinity of the graphite.

The first group of materials listed in Table VI is made up of samples of Santa Maria LV coke heat-treated to temperatures between about 1800 and about 2800°C. The graphitizing behavior of this material has been discussed in detail in Reports 11 and 12 in this series. The second group consists of heat-treated samples of Union Carbide Corporation's No. 1 needle coke, which were discussed in Report No. 14. The samples of the third group are from special carbons and graphites prepared for Sandia Laboratories by Ultra Carbon Corporation, by heat-treating segments of an extruded graphite rod. The final group represents samples of commercial graphite obtained from Dr. Meyer, which he has used in some of his own investigations.

From these results, it is evident that when carbons have been heat-treated to temperatures much above 1000°C, their hydrogen contents are low enough so that uncertainties in the chemical analyses may obscure the trend of hydrogen concentration. However, data for the series of Ultra Carbon samples are quite regular, and are probably typical. They show a large decrease in hydrogen content during baking between 800 and 1400°C, with little accompanying change in crystalline parameters. At 2200°C most of the hydrogen has been expelled. Much additional graphitization occurs between 2200 and 2900°C, with little further change in hydrogen analysis. It appears reasonable that most of the hydrogen loss should occur by pyrolysis during baking, which normally produces a highly disordered carbon, and that most of the organization of the carbon into a well-ordered graphite should occur at a temperature high enough so that little hydrogen remains to interfere with ordering.

Results for the Santa Maria coke suggest that the randomness of its structure interferes somewhat with hydrogen removal, as it does with ordering of the carbon. As would be expected, the initially better-organized needle coke graphitizes more readily and to a higher degree. However, it is not clear from the analytical results that this has affected its behavior with regard to hydrogen retention. The inconsistencies in hydrogen contents

TABLE VI
HYDROGEN CONTENTS AND CRYSTALLINE PARAMETERS OF COKES AND GRAPHITES

Sample Identi- fication	Material Description	Max. Ht-Trt Temp., °C	Hydro- gen Content, ppm ^(f)	Crystalline Parameters	
				d_{002} , Å	L_c , Å
CL-6(1833)	Santa Maria isotropic coke	1833	110	3.42	92
CL-6(2147)	Santa Maria isotropic coke	2147	150	3.394	187
CL-6(2468)	Santa Maria isotropic coke	2468	70	3.372	297
CL-6(2808)	Santa Maria isotropic coke	2808	40	3.367	323
CNL-1(1825)	Union Carbide needle coke	1825	130	3.418	217
CNL-1(2130)	Union Carbide needle coke	2130	70	3.395	280
CNL-1(2420)	Union Carbide needle coke	2420	110	3.374	427
CNL-1(2715)	Union Carbide needle coke	2715	60	3.362	670
UCS-A	Ultra Carbon Corp. Special Sample, Group A, No. 1	800	1400	3.435	32 ^(c)
UCS-B	Ultra Carbon Corp. Special Sample, Group B, No. 11	1400	290	3.430	35 ^(d)
UCS-C	Ultra Carbon Corp. Special Sample, Group C, No. 22	2200	20	3.410	218 ^(e)
UCS-E	Ultra Carbon Corp. Special Sample, Group E, No. 23	2485 ^(b)	35	3.362	570
UCS-D	Ultra Carbon Corp. Special Sample, Group D, No. 32	2900	35	3.361	580
---	POCO Grade AXF-QB	---	200	---	---
---	POCO. "New lot, 1/4-in. rod."	---	35, 25 ^(a)	---	---
---	Pfizer pyrolytic (pyroid). "Old Pfizer."	---	< 5	---	---
---	Pfizer pyrolytic. "New lot, 1/8-in. plate."	---	15, 10 ^(a)	---	---
---	Union Carbide SPK spectroscopic electrode.	---	30	---	---
---	Ultra Carbon U50-7, 1/4-in. rod.	---	15, 25 ^(a)	---	---
---	Union Carbide ATJ graphite, block.	---	30, 90 ^(a)	---	---

(a) Duplicate samples.

(b) Halogen purified.

(c) Contained about 10% crystalline graphite with $d_{002} = 3.363 \text{ Å}$ and $L_c = 235 \text{ Å}$.

(d) Contained about 8% crystalline graphite with $d_{002} = 3.364 \text{ Å}$ and $L_c = 280 \text{ Å}$.

(e) Composite value. Contained about 84% turbostratic material with $d_{002} = 3.410 \text{ Å}$, $L_c = 235 \text{ Å}$, and 16% crystalline graphite with $d_{002} = 3.364 \text{ Å}$, $L_c = 350 \text{ Å}$.

(f) Chemical analyses by LASL Group CMB-1.

among the tabulated values for the Santa Maria and Union Carbide cokes probably result from the fact that these samples were heat-treated in the atmospheres developed spontaneously within closed crucibles packed in carbon during heating, and not otherwise controlled. The Ultra Carbon samples were heat-treated in nitrogen, which evidently was a more consistent atmosphere, but may have resulted in lower hydrogen levels than would be considered normal.

Among the commercial graphites, the very low hydrogen contents of the pyrolytic graphites are noteworthy. The relatively high hydrogen content of POCO AXF-QB is consistent with the grade designation in indicating that the material has been impregnated and baked, but not subsequently regraphitized. The much lower hydrogen content of the "new lot" of POCO indicates that its final heat-treatment was to a relatively high temperature. The very low hydrogen content of the Ultra Carbon U50-7 rod suggests that, like the other Ultra Carbon samples, it was graphitized in a controlled atmosphere having a very low partial pressure of hydrogen.

V. QUANTIMET IMAGE-ANALYZING COMPUTER

(H. D. Lewis)

The Quantimet 720 is an automatic image analyzer marketed by IMANCO Division of Metals Research Corporation, intended for use in the quantitative analysis of the microstructural features observed in metallographic sections. A unit of this type was purchased some months ago by LASL Group CMB-5 and, in cooperation with Dana L. Douglass of CMB-5, assistance has been provided in putting it into operation, evaluating its performance, and developing data analysis methods for its outputs. It is of particular interest to CMB-13 because of its potential application to the characterization of particulates.

The Quantimet utilizes vidicon (video camera) sample scanning and a closed-circuit television display. The CMB-5 unit has an epidiascope sample processor for measurements on photographs. This is a peripheral unit which contains the vidicon scanner, a power supply, and a light source. The size of the field of view is

controlled by adjusting the optical lens system that transmits the image to the vidicon. The video signal is transformed to both a visual and a digital output in a central processing unit which consists of detector, programmer, computer, and video-display modules. The detector is essentially a gray-shading discriminator, covering the range black to white. Three independent, variable, threshold controls permit simultaneous measurements of four types of areas appearing as different shades of gray. The video display reproduces the overall appearance of the sample and, at the operator's option, superimposes on this image a second one identifying the features detected by the instrument.

The "live-frame" region represented by the video display is variable from one to 500,000 "picture points," with best-possible feature-detection sensitivity of the order of one or two points in 500,000. The resolving power of the system also depends on the magnification and quality of the photograph being examined and the resolution of the lens system transmitting the image to the vidicon.

Any of four measurement modes can be selected by the computer module: area, intercept, end-count, and full-feature count. In the area-measurement mode, the total area of a selected photographic feature or gray shade is determined as a number of picture points, or the total area of features either larger or smaller than a preselected size may be determined. In the intercept mode, a total intercept length (in picture points) is determined by counting the number of times the vidicon raster line intersects the leading edge of the selected feature. The two available "counting" modes are also "sizing" modes. The end-count mode detects all downward projections of features in the live frame. The full-feature mode detects and assigns one count to each resolvable feature; for example, either an isolated particle or a set of overlapping particles would be counted as one feature. The "size" of the feature is determined as the maximum horizontal chord length, in picture points. Unfortunately, this definition of particle diameter is unique, and is not the same as the measures of particle "size" commonly used in other optical sizing techniques.

After a protracted debugging period, the Quantimet was used successfully as a quantitative metallography tool to determine phase ratios in two-phase systems of interest to CMB-5. Attempts were then made to use it to estimate the bulk density of a graphite and to determine the carbide content of a graphite-ZrC composite.

The attempts at bulk-density measurement were not satisfactory. The values obtained were approximately 20% lower than that determined from sample weight and volume. Apparently this resulted primarily from over-detection of the black void areas in the dark gray graphite background. However, it is also true that, in calculating bulk density from the Quantimet output, it is assumed that the volume fraction of void is the same as the area fraction measured on a photograph of a two-dimensional section through the sample. Validity of this assumption depends upon the morphology of the three-dimensional pore structure, which was not investigated. In any case, with additional experience in this particular measurement, better estimates of the pore fraction can probably be obtained.

The attempt at carbide-concentration measurement on the graphite-ZrC composite indicated that the method would be useful both for quick estimation of average carbide content and for estimating uniformity of the carbide distribution. In the 250X photomicrograph examined, contrast between the detected feature, ZrC, and the graphite background was ideal. For a sample with a nominal ZrC content of 30 vol %, the average content calculated from the Quantimet output was 28.6 vol %. Uniformity of the dispersion could easily be determined by scanning several fields of view and calculating the standard deviation of the measurements.

With increased knowledge of the tricks in calibration and gray-shade discrimination, it is now possible to determine the fractional composition of a five-phase material. A computer program has been written for analysis of the Quantimet output for two to five phase areal analysis. It evaluates the fractional area occupied by each of one to five phases in up to twenty fields per photograph in a set of as many as twenty photographs representing twenty microscopic fields of view. The program

calculates the average fractional area and standard deviation in the area occupied for each phase in each photograph and for the entire set of photographs.

Although the main application of the Quantimet has been in phase analysis, D. L. Douglass has used it for a variety of measurement problems, including determination of the size of hardness-test indentations. The unit is of course useful for measurement of particle-size distributions. However, the usual problems in sample deagglomeration are more severe with the Quantimet because the detector cannot identify overlapping particle images. The automatic sizing and count operational mode which would be desirable for CMB-13 work is not possible with existing Quantimet modules. However, measurement of size distribution with "size" defined as projected particle area is possible if the adjustable "live-frame" is used to isolate and measure individual particles. This is tedious, but is perhaps more easily performed using the Quantimet than any other existing device.

An IMANCO representative indicates that a new computer module will soon be available for the Quantimet which will provide all of the above measurement modes plus pattern-recognition capability, particle-periphery measurement in count mode, and particle-area measurement in count mode. This should be of great value for high-speed particle sizing, and the use of area and periphery measurements in count mode may permit the statistical determination of a quantitative particle shape factor.

VI. PUBLICATIONS RELATING TO CARBONS AND GRAPHITES

- Reiswig, R. D., "Cathodic Vacuum Etching with Hydrogen," Metallographic Group, 1968, 22nd Meeting, San Diego, Calif., Technical Papers, pp. 162-7, DTIE, 1971.
- Smith, M. C., "CMB-13 Research on Carbon and Graphite, Report No. 18, Summary of Progress from May 1 to July 31, 1971," LA-4896-PR, March 1972.